

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Katsuhito MIURA et al.

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Title: CROSSLINKED POLYMER ELECTROLYTE AND USE THEREOF

DECLARATION UNDER 37 C.F.R. §1.132

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I, Katsuhito MIURA, a citizen of Japan, having an address of c/o DAISO CO., LTD., 12-18, Awaza 1-chome, Nishi-ku, Osaka-shi, OSAKA-fu, Japan declare and say as follows:

1. I am one of the co-inventors of the above-identified application.
2. I received the degree of Bachelor of Chemical Engineering from Nagasaki University, Nagasaki, Japan in 1983, and the degree of Doctor of Engineering Science from Osaka University in 1994 on the study of "Polymerization Mechanism of Polyether".
3. I have been employed by Daiso Co., Ltd. from 1983 to the present, and have been engaged in research on opening polymerization of oxirane compounds.
4. The experiments discussed below were carried out under my supervision.

In the following Experiments, the present invention was compared with Kohjiya et al. (USP 5,837,157) and Miura et al. (USP 6,159,389).

Experiment 1 (according to the present invention)

The polymer was prepared in the same manner as in Polymerization Example 1 of the present Description. That is, the polymer was prepared as follows:

[Preparation of polymer]

After the atmosphere in a four-necked glass flask (internal volume: 3 L) was replaced by nitrogen, the condensate (2 g) obtained in the above Preparation Example as a catalyst, glycidyl methacrylate (60g) having a water content adjusted to not more than 10 ppm and n-hexane (1,000 g) as a solvent were charged in the flask. Ethylene oxide (195 g) was gradually added with monitoring the conversion of glycidyl methacrylate by gas chromatography. The polymerization reaction was terminated by using methanol. A polymer was isolated by decantation, dried at 40°C under a normal pressure for 24 hours, and then dried at 45°C under reduced pressure for 10 hours to give 207 g of the copolymer (hereinafter referred to as "Present Copolymer"). ^1H NMR spectrum analysis revealed that the composition in terms of monomer of this copolymer had ethylene oxide of 93 mol% and glycidyl methacrylate of 7 mol%.

[Crosslink test]

Present Copolymer was crosslinked in almost the same condition recited in Example 1 of the present Description. That is, the polymer was crosslinked as follows:

1 g of the binary copolymer obtained above, 10 g of ethylene carbonate, 10g of γ -butyrolactone [given amounts of ethylene carbonate/ γ -butyrolactone (50/50)], 0.05 g of benzoyl peroxide as a radical initiator and 2 g of LiBF₄ were homogeneously mixed to give a mixture liquid. This mixture liquid was coated on a separator with a double-sided coater and impregnated into a separator, and was kept at 90°C for 10 hours to produce a crosslinked polymer electrolyte composition (hereinafter referred to as "Present Electrolyte") having the thickness of 40 micrometers.

[Battery test]

Present Electrolyte was subjected to a battery test which is almost the same as in Example 3 of the present Description. That is, Present Electrolyte was tested as follows:

(Preparation of Positive Electrode)

90 g of lithium cobaltate, 4 g of acetylene black, 6 g of polyvinylidene fluoride and 100 g of dimethyl formamide were mixed by a disper and coated on an aluminum foil (thickness: 25 micrometers). The solvent was removed by the drying under reduced pressure. The mixture was pressed by two rolls, dried under reduced pressure, and maintained in a glove box under an argon environment.

(Preparation of Negative Electrode)

90 g of graphite powder and 10 g of polyvinylidene fluoride were dissolved and dispersed in 80 g of N-methyl pyrrolidone to produce a negative electrode active substance slurry. The negative electrode active substance

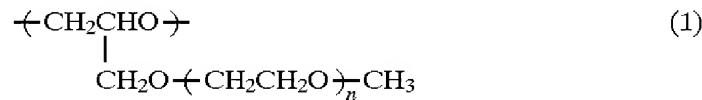
slurry was coated on a surface of a copper foil, dried and pressed by two rolls to produce a negative electrode.

(Preparation and Test of Battery)

A battery was assembled in a glove box under argon atmosphere by using the crosslinked polymer electrolyte composition having the separator, and positive and negative electrodes prepared by impregnating both of the positive electrode and the negative electrode with the mixture liquid obtained in the Crosslink test and conducting the thermal crosslinking. The assembled cell was kept in a constant temperature bath at 20°C for 12 hours, and the charge/discharge properties of the battery were examined. After the charge was conducted at a constant electrical current and a constant electrical voltage of 4.2 V at 60°C, the discharge to 3 V was conducted at a constant electrical current.

Experiment C1 (according to Kohjiya et al. (USP 5,837,157))

The copolymer of Example 2 of Kohjiya et al. (USP 5,837,157), that is, a polyether copolymer (hereinafter referred to as "Kohjiya Copolymer") of ethylene oxide (90 mol%) and the structural unit of the formula (1):



(10 mol%) was obtained.

The Kohjiya Copolymer was subjected to the Crosslink test.

Experiment C2 (according to Miura et al. (USP 6,159,389))

The polymer was prepared in the almost same manner as in Example 3 of Miura et al. (USP 6,159,389). That is, the polymer was prepared as follows:

[Preparation of polymer]

After the atmosphere in a four-necked glass flask (internal volume: 3 L) was replaced by nitrogen, the condensate of tributyltin chloride and tributyl phosphate (2 g) as a catalyst, epichlorohydrin (56 g), glycidyl methacrylate (20 g) having a water content adjusted to not more than 10 ppm and n-hexane (1,000 g) as a solvent were charged in the flask. Ethylene oxide (175 g) was gradually added with monitoring the conversion of epichlorohydrin by gas chromatography. The polymerization reaction was conducted at 20°C for 20 hours. The polymerization reaction was terminated by using methanol. The polymer was isolated by decantation, dried at 40°C under a normal pressure for 24 hours, and then dried at 45°C under reduced pressure for 10 hours to give 185 g of a polymer (hereinafter referred to as "Miura Copolymer").

¹H NMR spectrum analysis revealed that the composition in terms of monomer of this copolymer had ethylene oxide of 84 mol%, epichlorohydrin of 13 mol% and glycidyl methacrylate of 3 mol%.

The Miura Copolymer was subjected to the Crosslink test to give a polymer electrolyte and subjected to the Battery test.

The results of the Crosslink test and the Battery test are shown in Table 1 and Table 2.

[Polymer]

The present invention:

Ethylene oxide/Glycidyl methacrylate=93/7 (Polymerization Example 1)

Kohjiya et al. (USP 5,837,157):

Ethylene oxide/Formula (1) (n=2) = 90/10 (Example 2)

Miura et al. (USP 6,159,389):

Ethylene oxide/Epichlorohydrin/Glycidyl methacrylate = 84/13/3 (Example 3)

Table 1

Electrolyte solution amount (parts by weight, based on 100 parts by weight of polymer)	100 pbw	5,000 pbw	10,000 pbw
Experiment 1 (Present invention)	Gelation	Gelation	Gelation
Experiment C1	Liquid (oily)	Liquid	Liquid
Experiment C2	Gelation	Liquid	Liquid

Since Experiment C1 [Kohjiya et al. (USP 5,837,157)] did not contain a crosslinking monomer, the crosslink test did not give a crosslinked polymer solid electrolyte.

In Experiment C2 [Miura et al. (USP 6,159,389)], the crosslink (gelation) was not caused in the case of electrolyte solution amount of 5,000 pbw or 10,000 pbw.

Table 2

Electrolyte solution: 100 parts by weight

	Initial discharge capacity	Discharge capacity after 10 cycles
Experiment 1 (Present invention)	121 mAh/g	118 mAh/g
Experiment C2	103 mAh/g	65 mAh/g

When the battery test is performed in the same conditions, the crosslinked polymer solid electrolyte of Experiment C2 [Miura et al. (USP 6,159,389)] has a low initial discharge capacity and has significant decrease of discharge capacity after 10 cycles.

Example 3 in the present Description indicates has an initial discharge capacity of 142 mAh/g as shown in the present application, since the amount of the electrolyte solution is 2,000 parts by weight, based on 100 parts by weight of the polymer. In this Experiment 1 (Present invention), the initial discharge capacity was 121 mAh/g, since the amount of the electrolyte solution was changed to 100 parts by weight, based on 100 parts by weight of the polymer.

As shown above, the present invention has significantly excellent effects in comparison with Kohjiya et al. (USP 5,837,157) and Miura et al. (USP 6,159,389).

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S. Code 1001 and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

Date: _____

Katsuhito MIURA